



Facile synthesis of flower-like PbO as a precursor to form nanodendritic PbO₂ for positive active material (PAM) of lead-acid electrochemical storage devices



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ARTICLE INFO

Article history:

Received 4 March 2014

Accepted 19 April 2014

Available online 26 April 2014

Keywords:

Nanodendritic PbO₂

Flower-like PbO

Nanoparticles

Lead-acid battery

Lead-acid hybrid supercapacitor

Energy storage and conversion

ABSTRACT

Nanodendritic PbO₂ has been the attractive electrode material with unique morphology and enhanced electrochemical performance for lead-acid electrochemical storage devices. However, numerous studies have only investigated this unique material via electrodeposition technique. In this paper, flower-like PbO consisting three dimensional (3D) nanoflakes was successfully synthesized and used as a starting precursor to form nanodendritic PbO₂ via electrochemical oxidation at constant voltage. The improved electrochemical results displayed by the formed nanodendritic PbO₂ in cyclic voltammetry (CV) and initial discharge capacity, which is able to deliver 170 mA h g⁻¹ at 200 mA g⁻¹, is significantly suggesting that the formation of nanodendrites on the primary surface of agglomerated PbO₂ provides larger crystallite network structures for better material utilization at high discharge rate.

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1. Introduction

Lead-acid electrochemical storage devices [LAESD], such as lead-acid battery and hybrid supercapacitor, are believed to be the suitable candidates for application in hybrid electric vehicle (HEV) to fulfill the economic cost and performance objectives as part of the efforts to mitigate the worsening condition of global warming effects [1]. Despite the pros and cons reported on LAESD in HEV application [2], many researchers around the world accept that electrode materials with unique microstructural parameters will be the key solution to the problem [3].

Recently, there has been a rising interest in synthesizing 3D dendritic nanostructures of PbO₂ to be the electrode material in LAESD, which is proven to have enhanced electrochemical performance as the dendritic nanostructure is significantly large in surface area for high charge and mass transports [3]. Due to difficulties in investigating the microstructural parameters of PbO₂ in commercial lead-acid batteries, numerous studies have only focused on electrodeposition technique to produce various microstructural parameters of PbO₂ for performance evaluation [4] including the formation of nanodendritic PbO₂ [5,6]. Thus far, there has never been a report

indicating the desired material can be prepared via electrochemical oxidation of active paste (basic lead sulfate) which is produced by using PbO as the starting precursor.

Consequently, in this paper, we demonstrate a facile synthesis of flower-like PbO via one-pot chemical synthesis method by reacting lead(II) nitrate solution (Pb(NO₃)₂) with sodium hydroxide solution (NaOH) without the presence of any structure-director additives under vigorous stirring condition at room temperature. The as-synthesized PbO is later applied to produce active paste for electrochemical oxidation in 4.7 M sulfuric acid (H₂SO₄) to form nanodendritic PbO₂. Unlike electrodeposition, this technique is readily implementable in the manufacturing process of lead-acid battery or other LAESD processes to economically obtain the desired microstructures of electrode material with enhanced electrochemical performance. Moreover, the improved electrochemical results of nanodendritic PbO₂ were compared with those of bulk PbO₂ particles formed by using commercial pure PbO as the starting precursor.

2. Experimental

Pb(NO₃)₂ solution was prepared and reacted with NaOH solution at a molar ratio [Pb(NO₃)₂:NaOH] of 0.4 under vigorous stirring by magnetic bar for 15 min. The yellow greenish precipitate was filtered and washed with excess acetone before drying in

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an oven at 50 °C for 24 h. The X-ray diffraction (XRD) of dried powder was characterized by using an X-ray diffractometer X'PERT PRO PW3040 (Cu K α radiation and wavelength, $\lambda=0.154$ nm) for product quality and scanning electron microscopy (SEM) by FEI Quanta-400 FESEM for microstructural analysis.

The as-synthesized PbO was later mixed with DI water and 4.7 M H₂SO₄ at a stated weight ratio [PbO:DI water:H₂SO₄=10:3:1] to produce active mixture for pasting onto a lead alloy cavity of 0.5 cm² as electrode, and followed by drying in an oven at 50 °C for 24 h. The dried electrode was used as positive electrode and soaked into 4.7 M H₂SO₄ for 2 h prior to electrochemical oxidation at constant voltage of 2.48 V for 48 h [7] to form PbO₂. The formed PbO₂ was cleaned with excess acetone for XRD and SEM analyses. Same processes were repeated for commercial PbO supplied by Yokohama Batteries, Malaysia.

Electrochemical tests were conducted by using Autolab PGSTAT302N in a classical three-electrode cell containing 4.7 M H₂SO₄ where the formed PbO₂ was used as the working electrode, while platinum mesh as the counter electrode and Hg/Hg₂SO₄/K₂SO₄ (sat.) as the reference electrode. CV measurements were conducted at a scanning rate of 10 mV s⁻¹ from 0.6 to 1.6 V. Meanwhile, the initial discharge behavior was investigated by discharging the working electrode at a current density of 200 mA g⁻¹ until its potential decreased to 0.65 V. All experiments were carried out at room temperature unless stated otherwise.

3. Results and discussion

Structure and morphology: Fig. 1a and b show the XRD patterns of as-synthesized PbO and commercial pure PbO respectively. Both diffraction peaks can be perfectly indexed to that of pure PbO with a mixture of orthorhombic and tetragonal structures. β -PbO (orthorhombic) is mostly observed in Fig. 1a while majority of α -PbO (tetragonal) can be seen in Fig. 1b. As opposed to conventional chemical synthesis of nanostructured PbO [7,8], the presence of structure-director additives and heating process to decompose lead hydroxide (Pb(OH)₂) to PbO are not necessary as the synthesis medium is always maintained at pH 14 for the transformation of unstable Pb(OH)₂ to pure PbO in high pH medium [9] due to lower molar ratio of Pb(NO₃)₂ to NaOH, which is compatible to the result presented in Fig. 1a.

Meanwhile, Fig. 1c and d represent the XRD of nanodendritic PbO₂ (electrochemically oxidized from active mixture of as-synthesized PbO) and bulk PbO₂ particles (electrochemically oxidized from active mixture of commercial pure PbO), respectively. Both samples contain majority of β -PbO₂ while small amount of α -PbO₂ and lead sulfate (PbSO₄) are observed. All four distinctive diffraction peaks in Fig. 1 have indicated that the samples are highly crystalline.

On the other hand, Fig. 2a and b are illustrating SEM images of as-synthesized PbO and commercial pure PbO. As can be seen in Fig. 2a, the flower-like PbO is formed with 3D networks of nanoflakes. The thickness of each nanoflake ranges from 250 to 280 nm is seen in higher magnification of SEM image (inset of Fig. 2a), while its length is from 2 to 36 μ m. The formation of nanoflake PbO leading to the growth of flower-like structure is anisotropic. The growth mechanism of nucleic proceeds spontaneously with high activation energy according to periodic bond chain (PBC) theory [10] where flat crystal growth is dependent on a discontinuous surface [11]. Besides that, lumps of PbO particles ranging from 250 nm to 10 μ m can be seen in Fig. 2b.

Furthermore, Fig. 2c is depicting SEM image of nanodendritic PbO₂. The inset of Fig. 2c demonstrates that uniform nanodendrites are formed on the agglomerated PbO₂ with each diameter less than 50 nm. The growth of nanodendrites on the primary

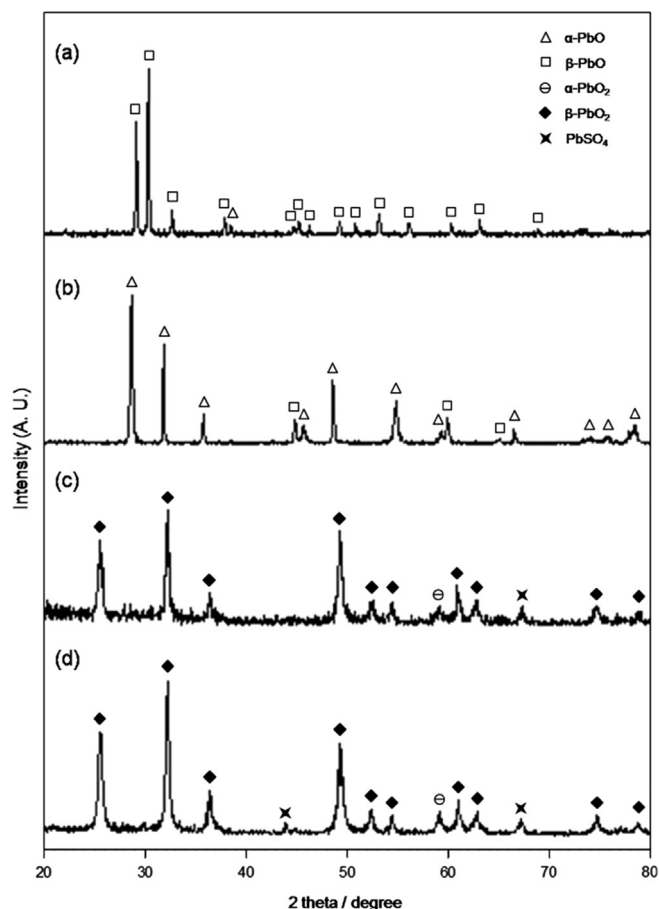


Fig. 1. XRD patterns of (a) as-synthesized PbO (prepared without the structure-director additive) and (b) commercial pure PbO, (c) nanodendritic PbO₂ (electrochemically oxidized from active mixture of as-synthesized PbO) and (d) bulk PbO₂ particles (electrochemically oxidized from active mixture of commercial pure PbO).

surface of agglomerated PbO₂ in Fig. 2c suggests that flower-like PbO, which is formed from crystal growth of discontinuous surface, when it is subject to electrochemical oxidation at constant voltage in the presence of electrolyte, the growth mechanism of nanodendrites would follow an adapted diffusion limited growth pattern model [12] where random particles would grow on a seed particle preferentially and anisotropically leading to the formation of uniform nanodendritic PbO₂. Meanwhile, only bulk PbO₂ particles are formed without dendritic rods after the electrochemical oxidation process, which can be observed in Fig. 2d when commercial pure PbO is used as the starting precursor.

Electrochemical behaviors of prepared samples: Fig. 3a displays the cyclic voltammograms of nanodendritic PbO₂ and bulk PbO₂ particles in 4.7 M H₂SO₄ at 20th cycle respectively. The CV tests were conducted at a scanning rate of 10 mV s⁻¹ in the potential range of 0.6–1.6 V. The obtained CV curves are similar to those acquired elsewhere [13]. The oxidation of PbSO₄ to PbO₂ can be observed at the anodic peak of 1.4 V (VS. Hg/Hg₂SO₄ in sat. K₂SO₄), while the oxidation of oxygen occurs beyond 1.5 V, followed by the reduction of PbO₂ to PbSO₄ at the cathodic peak of 0.93 V. The curves show that the cathodic current is much higher than the anodic current. By comparison, the CV curve of nanodendritic PbO₂ exhibits higher current density than that of bulk PbO₂ particles and this might be attributed to high surface area and better network contact of nanodendritic particles for fast charge transfer [5].

Other than that, Fig. 3b shows the first discharge capacity curves of nanodendritic PbO₂ and bulk PbO₂ particles, which are

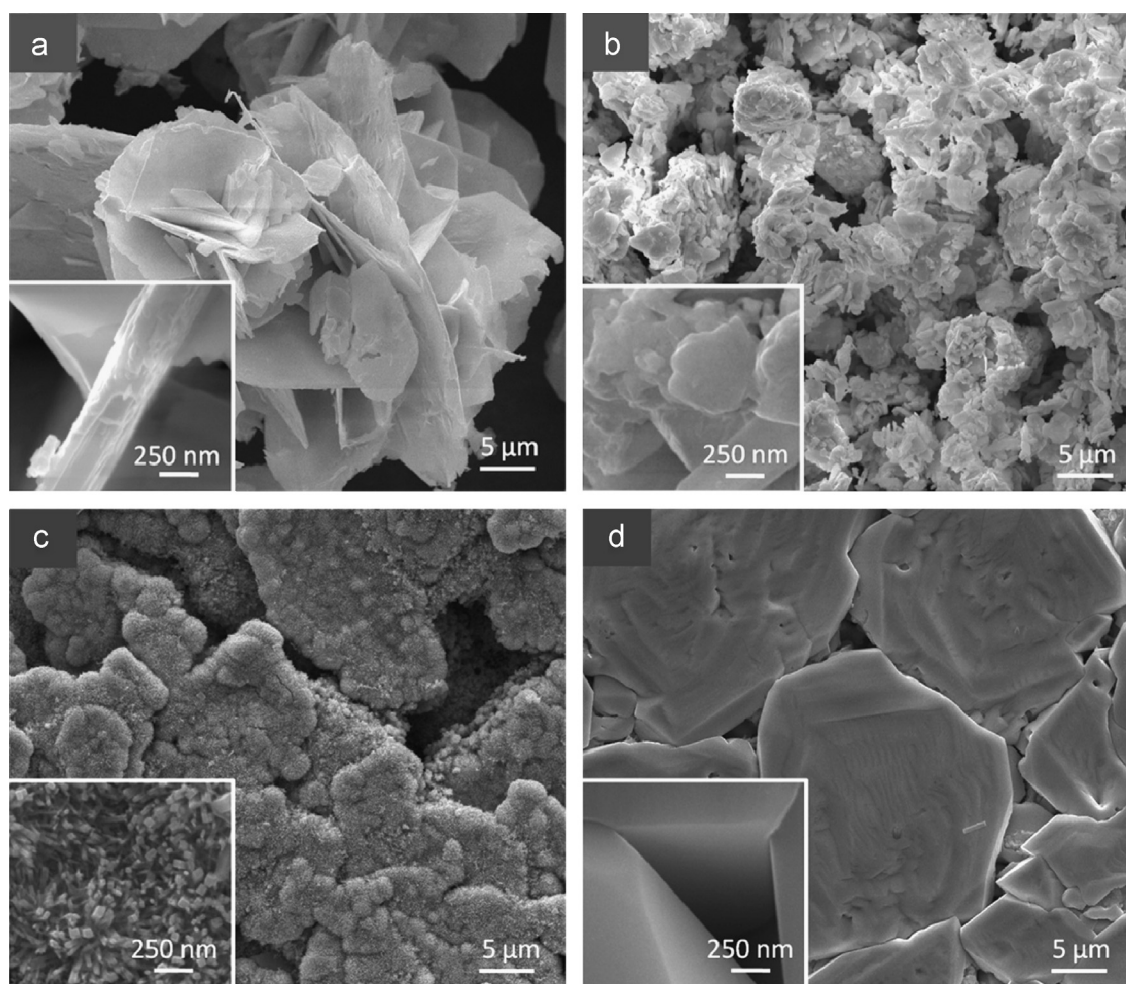


Fig. 2. SEM images of (a) as-synthesized flower-like PbO, (b) commercial pure PbO, (c) nanodendritic PbO₂, and (d) bulk PbO₂ particles.

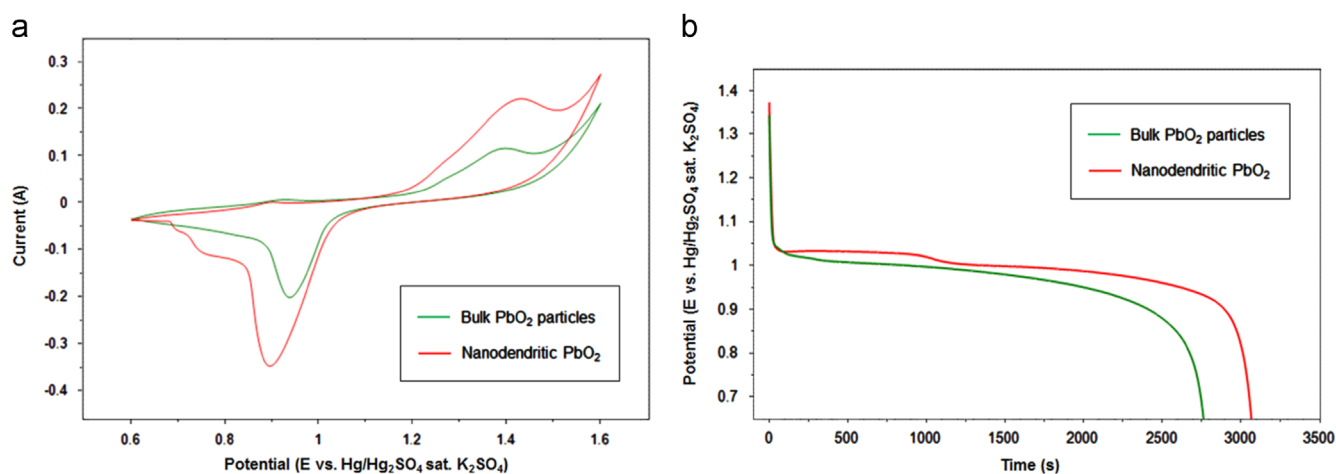


Fig. 3. (a) Cyclic voltammetry performed at scanning rate of 10 mV s⁻¹ and (b) first discharge capacity curves for both nanodendritic PbO₂ and bulk PbO₂ particles respectively.

performed at a current density of 200 mA g⁻¹ and cut-off voltage of 0.65 V in 4.7 M H₂SO₄. As 50 mg of active mixture was initially applied for both samples respectively to form PAM, the first discharge capacity figure of nanodendritic PbO₂ indicates that the acquired capacity is 170 mA h g⁻¹, while bulk PbO₂ particles is 153 mA h g⁻¹. The improved results suggest that the formation of nanodendrites on the primary surface of agglomerated PbO₂ provides larger crystallite network structures for better material

utilization at high discharge rate despite it is the first discharge cycle.

4. Conclusion

In summary, the flower-like PbO consisting 3D nanoflakes was successfully synthesized via simple chemical synthesis method

and used to form nanodendritic PbO_2 as PAM for LAESD. This work can help identify the essential unique morphology of starting precursor, where its crystal growth is dependent on discontinuous surface, can be used as a substrate to form nanodendritic material with better network structure via electrochemical oxidation at constant voltage. Cycling test of discharge capacity for the material will be further investigated while present results show that it can be a promising electrode material for improving commercial LAESD with the desired microstructure.

Acknowledgements

The author would like to thank Yokohama Batteries (Malaysia) Sdn. Bhd. for all the supports provided and especially to CEO of the company, Dr. Patrick Yong Mian Thong, for his in-depth knowledge of lead-acid batteries leading to the success of this project. Additional resources from MOE (FRGS/2/2013/SG02/UNIM/02/1), UNMPUCRG (UNR40001), MOSTI-eScienceFund (M0061.54.01/NMR40003), HIR-Chancellory (UM.C/625/1/HIR/079), HIR-MOHE

(UM.C/625/1/HIR/MOHE/SC/06) and UMRG (RP007B/13AFR) are also acknowledged.

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